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Organometallic coordination polymers: Sn(IV) derivatives with the bis(triazolyl)methane ligand

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ABSTRACT

Several alkyl- or aryl-tin(IV) halides of general formula SnR_nX_{4-n} (n = 0–2; R = Me, Et, ^{n}Bu, ^{t}Bu, Ph; X = Cl, Br), possessing Lewis acidic character, have been reacted with the polydentate N-donor ligand bis(1,2,4-triazolyl)methane (Btm), affording $Btm(SnR_nCl_{4-n})$ complexes. $(Btm)_2Sn^nBu_2Br_2$ and $(Btm)Sn^nBu_2(NO_3)_2$ are also reported. These materials were characterized by elemental analyses, IR and ^1H (and, in selected cases, ^{119}Sn) NMR spectroscopy, and, were possible, *ab initio* X-ray powder diffraction methods. The crystal structures determined by the latter method showed that Btm ligands, in the exobidentate mode, link Sn(IV) fragments which lie 9.5–11.2 Å apart (depending on the Btm conformation and on the local metal stereochemistry), in one-dimensional chains packed in parallel bundles. The main geometrical features of these 1D polymers are compared with those of the bis(imidazolyl)methane complexes and of the known Btm derivative, $Btm(Ph_2SnBr_2)$. Interestingly, the expected isomorphous structures for selected couples was not found, as if very subtle energetic differences were driving the crystallization of these species into different structure types.

1. Introduction

In the last decades, one-dimensional coordination polymers have been the subject of several investigations, for their peculiar structures, reactivity and functional activity, which have been often attributed to the cooperativity of the different metal coordination spheres, enhancing, or generating, new functional properties [1]. This is particularly true if the metal arrangement is nearly colinear, as beautifully demonstrated by the Fe(II) spin crossover systems (showing hysteretic behavior near RT) [2], the Cu(II) pyrazolate (vapochromic) polymers [3,4] and, long time ago, by the electron-conducting (doped) $K_2Pt(CN)_4$ materials [5]. Less investigated are monodimensional *organometallic* polymers, some of which could be characterized by X-ray powder diffraction (XRPD) methods only, eventually disclosing new, or unexpected, connectivity, conformation and stoichiometry. For example, the elusive structures of the $[Ru(CO)_4]_n$ [6], $[Ru(2,2'\text{-bipyridine})(CO)_2]_n$ [7], $[PdCl(acetonyl)]_n$ [8], $[HRe(CO)_4]_n$ and $[HRe(CO)_4]_6$ [9] species were all determined from laboratory XRPD data on less-than-ideal polycrystalline materials, not affording single-crystals of suitable quality.

Recently, our interest has shifted from carbonylic species to new polytopic ligands, capable of bridging metal centers at different distances, thanks to the exobidentate mode of N-heterocyclic rings, such as pyrazolates, imidazolates and pyrimidinolates. A partial summary of our studies can be found in Refs. [10–12]. Worthy of note, among the many species prepared during this ongoing project, interesting functional materials could be prepared: molecular magnets [13]; second harmonics generation-active polymers [14]; nanoporous MOFs with high gas storage capacity and size-selective catalytic activity [15].

Our latest results were focused on the coordination chemistry of the new bis(imidazolyl)methane ligand [16] (Bim, see Scheme 1), which was coupled to a number of metal centers: transition metal ions (Rh, Zn, Cd and Hg) [17–19] and main group elements (Sn) [20]. This recent work of ours has been substantially augmented by the publications of Chen and Cui, who used also other transition metal ions [Ag(I), Mn(II) Fe(II), Co(II), Ni(II) and Cu(II)], also in combination with complex carboxylates [21–23]. Aiming at better comprehending the subtle factors driving the formation of these polymers, in the last year we shifted our attention to the similar bis(1,2,4-triazolyl)methane ligand (Btm, see Scheme 1), which, bearing two additional nitrogen atoms on the heterocyclic ring, may show an increased flexibility and coordination versatility.

As an initial set of compounds, we prepared Sn(IV) organometallic polymers, to be structurally compared with the Bim analogs

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reported by us in Ref. [20]. Indeed, organotin polymers are increasingly attracting the attention of many for their potential industrial application and biological activities [24,25], since they are effective against wood decay fungi and marine borers but also widely used in self-polishing paints [26]. On the other hand, 1,2,4-triazole is associated with diverse pharmacological activities such as analgesic, antiasthmatic, diuretic, antihypersensitive, anticholinergic, antibacterial, antifungal and anti-inflammatory activity [27–31] and, thanks to the presence of the pyridinic nitrogen atoms, is able to form metal coordination polymers, of still unknown structure [32], or fully characterized, as in the recently reported lead acetate and hydroxo-copper derivatives [33,34]. Thus, a combination of these two functions within the same compound may, in principle, lead to an increasing antimicotic effect.

The modification of poly(pyrazolyl)alkane ligands through replacement of the pyrazolyl by a triazolyl ring has been originally performed by Elguero and coworkers in 1982 [35]. Unfortunately, the coordination chemistry of Btm is still poorly developed, mainly due to the lack of conventional single-crystal structural analyses, as a consequence of the poor solubility of its (likely polymeric) metal complexes. In this contribution, we present the synthesis of several Btm-based organotin polymers, a few of which have been structurally characterized using state-of-the-art (less conventional) structural methods (employing laboratory X-ray powder diffraction data), coupled to ancillary elemental, IR and ^{1}H and ^{119}Sn NMR analyses. Our results will be compared with those reported by Tang et al. who described the crystal and molecular structure of the polymeric Btm(Ph$_2$SnBr$_2$) derivative [36]. In order to improve the legibility of this paper, also in conjunction with the previously communicated results, the complete labeling and naming of the Sn(IV) polymers is hereafter reported:

Btm(SnMe$_2$Cl$_2$), $\mathbf{1_{Btm}}$
Btm(SnEt$_2$Cl$_2$), $\mathbf{2_{Btm}}$
Btm(Sn^{n}Bu$_2$Cl$_2$), $\mathbf{3_{Btm}}$
Btm(SnPh$_2$Cl$_2$), $\mathbf{4_{Btm}}$
Btm(SnMeCl$_3$), $\mathbf{5_{Btm}}$
Btm(SnPhCl$_3$), $\mathbf{6_{Btm}}$
Btm(Sn^{t}Bu$_2$Cl$_2$), $\mathbf{7_{Btm}}$
Btm(SnCl$_4$), $\mathbf{8_{Btm}}$
Btm(SnBr$_4$), $\mathbf{9_{Btm}}$
(Btm)$_2$Sn^{n}Bu$_2$Br$_2$, $\mathbf{10_{Btm}}$
BtmSn^{n}Bu$_2$(NO$_3$)$_2$, $\mathbf{11_{Btm}}$

while the bis(imidazolyl)methane (Bim) analogs will be referred to by the corresponding $\mathbf{X_{Bim}}$ labels.

2. Experimental

2.1. Materials and methods

All chemicals and reagents were of reagent grade quality and were used as received without further purification. All solvents were distilled prior to use. Dichloromethane was freshly distilled from CaH$_2$. Other solvents were dried and purified by standard procedures. The samples were dried in vacuo to constant weight (293 K, 0.1 Torr). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNSO-elemental analyzer. IR spectra from 4000 to 370 cm^{-1} were recorded with a Perkin–Elmer Spectrum One FT-IR instrument. The solid samples were analyzed on the single reflection ATR accessories. The solid has been placed on the crystal area, the pressure arm being positioned over the crystal/sample area. IR spectra from 700 to 150 cm^{-1} were recorded with a Perkin–Elmer System 2000 FT-IR instrument. ^{1}H and ^{119}Sn NMR solution spectra were recorded on a Mercury-Plus Varian 400 NMR spectrometer (400 for ^{1}H and 149.2 MHz for ^{119}Sn, respectively). Referencing is relative to TMS (^{1}H) and Me$_4$Sn (^{119}Sn). NMR samples were prepared by dissolving a suitable amount of compound in 0.5 ml of solvent. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; and multiplet, m. Melting points are uncorrected and were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus.

2.2. Syntheses

2.2.1. Btm

The ligand Btm has been prepared by the literature methods [37], and has been recrystallized from hot chloroform. Mp 165–168 °C. *Anal.* Calc. for C$_5$H$_6$N$_6$: C, 40.00; H, 4.03; N, 55.97. Found: C, 40.02; H, 4.20; N, 56.03%. IR (nujol, cm^{-1}): 3181br, 3115w, 3106w, 1555w, 1508m, 1500m 391m, 383m, 360w br, 279w. ^{1}H NMR (CDCl$_3$, 293 K): δ, 6.44 (s, 2H, C$H_{2\mathrm{Btm}}$), 7.99 (s, 2H, CH_{Btm}), 8.42 (s, 2H, CH_{Btm}). ^{1}H NMR (CD$_3$OD, 293 K): δ, 6.68 (s, 2H, C$H_{2\mathrm{Btm}}$), 8.03 (s, 2H, CH_{Btm}), 8.80 (pt, 2H, CH_{Btm}). ^{1}H NMR (DMSO-d_6, 293 K): δ, 6.7 (s, 2H, C$H_{2\mathrm{Btm}}$), 8.1 (s, 2H, CH_{Btm}), 8.9 (pt, 2H, CH_{Btm}). ^{1}H NMR (acetone-d_6, 293 K): δ, 6.7 (s, 2H, C$H_{2\mathrm{Btm}}$), 8.1 (s, 2H, CH_{Btm}), 8.9 (pt, 2H, CH_{Btm}).

2.2.2. Btm(SnMe$_2$Cl$_2$) ($\mathbf{1_{Btm}}$)

To a stirred ethanol solution (20 mL) of Me$_2$SnCl$_2$ (0.219 g, 1.0 mmol) was added an ethanol solution (20 mL) of bis(triazol-1-yl)methane (Btm) (0.150 g, 1.0 mmol). The solution was stirred for 48 h under N$_2$ at room temperature. Upon diethyl ether addition a colorless precipitate formed which was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of diethyl ether and shown to be compound $\mathbf{1_{Btm}}$ (0.332 g, 0.90 mmol, yield 90%). M.p. 167–171 °C dec. *Anal.* Calc. for C$_7$H$_{12}$Cl$_2$N$_6$Sn: C, 22.73; H, 3.27; N, 22.72. Found: C, 22.93; H, 3.34; N, 22.70%. IR (nujol, cm^{-1}): 3117w, 3060w; 1547m, 1538m, 1502m υ(C$\cdots$C, C$\cdots$N), 353m, 205m, 175m, 575m υ(Sn–C), 240s br υ(Sn–Cl). ^{1}H NMR (DMSO-d_6, 293 K): δ, 1.04 (s, 6H, C$H_{3\mathrm{Sn}}$, $^{1}J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$: 114 Hz; $^{1}J(^{117}\mathrm{Sn}-^{1}\mathrm{H})$: 109 Hz), 6.7(s, 2H, C$H_{2\mathrm{Btm}}$), 8.0 (s, 2H, C$H_{\mathrm{Btm}}$), 8.9 (s, 2H, C$H_{\mathrm{Btm}}$). ^{1}H NMR (acetone-$d_6$, 293 K): δ, 1.2 (s, 6H, C$H_{3\mathrm{Sn}}$, $^{1}J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$: 84 Hz; $^{1}J(^{117}\mathrm{Sn}-^{1}\mathrm{H})$: 80 Hz), 6.7 (s, 2H, C$H_{2\mathrm{Btm}}$), 7.9 (s, 2H, C$H_{\mathrm{Btm}}$), 8.7 (s, 2H, C$H_{\mathrm{Btm}}$). ^{119}Sn NMR (CDCl$_3$, 293 K): +110 ppm. Λ_{m} (DMSO, 293 °C): 9.4 μS (1.0×10^{-3} M).

2.2.3. Btm(SnEt$_2$Cl$_2$) ($\mathbf{2_{Btm}}$)

Btm (0.158 g, 1.0 mmol) was added to a methanol solution (20 mL) containing Et$_2$SnCl$_2$ (0.247 g, 1.0 mmol). The solution was stirred for 5 days under N$_2$ at room temperature. Slow evaporation of the solution yields colorless crystals which were filtered, dried in vacuum and shown to be compound $\mathbf{2_{Btm}}$ (0.120 g, 0.30 mmol, yield 30%). M.p. 178–180 °C dec. *Anal.* Calc. for C$_9$H$_{16}$Cl$_2$N$_6$Sn: C, 27.17; H, 4.05; N, 21.12. Found: C, 27.23; H, 4.21; N, 21.03%. IR (nujol, cm^{-1}): 3140w, 3116w; 1513m υ(C$\cdots$C, C$\cdots$N), 535m, 485br, 373m, 289m, 279m, 267m, 245sh, 226sh υ(Sn–Cl). ^{1}H NMR (CDCl$_3$, 293 K): δ, 1.45 (t, 6H, C$H_{3\mathrm{Sn}}$, $^{3}J(\mathrm{Sn}-^{1}\mathrm{H})$: 170 Hz, 1.77 (q, 4H, C$H_{2\mathrm{Sn}}$, $^{2}J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$: 88 Hz), 6.44 (s, 2H, C$H_{2\mathrm{Btm}}$), 7.99 (s, 2H, C$H_{\mathrm{Btm}}$), 8.42 (s, 2H, C$H_{\mathrm{Btm}}$). ^{1}H NMR (CD$_3$OD, 293 K): δ, 1.38 (t, 6H, C$H_{3\mathrm{Sn}}$, $^{3}J(\mathrm{Sn}-^{1}\mathrm{H})$: 170 Hz), 1.67 (q, 4H, C$H_{2\mathrm{Sn}}$, $^{2}J(\mathrm{Sn}-^{1}\mathrm{H})$: 88 Hz), 6.67 (s, 2H, C$H_{2\mathrm{Btm}}$), 8.03 (s, 2H, C$H_{\mathrm{Btm}}$), 8.79 (s, 2H, C$H_{\mathrm{Btm}}$). ^{119}Sn NMR (CDCl$_3$, 293 K): +121 ppm. Λ_{m} (DMSO, 293 °C): 7.3 μS (1.0×10^{-3} M).

2.2.4. Btm(Sn^{n}Bu$_2$Cl$_2$) ($\mathbf{3_{Btm}}$)

Btm (0.150 g, 1.0 mmol) was added to a dichloromethane solution (20 mL) containing ^{n}Bu$_2$SnCl$_2$ (0.303 g, 1.0 mmol). The solution was stirred overnight. Upon addition of diethyl ether a colorless precipitate formed which was filtered off and washed with 20 ml of *n*-hexane and shown to be compound $\mathbf{3_{Btm}}$ (40% yield). From the mother liquor very small colorless crystals were also obtained that were identified as $\mathbf{3_{Btm}}$. M.p. 94–95 °C dec. *Anal.* Calc. for $C_{13}H_{24}Cl_2N_6Sn$: C, 34.40; H, 5.33; N, 18.51. Found: C, 34.24; H, 5.55; N, 18.34%. IR (KBr, cm^{-1}): 3115w, 3022w, 2970w, 2923w, 2909w; 1512m υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 1446w, 1399w, 1277m, 1195m, 1114s, 1020m, 982m, 951m, 916w, 778m, 736s, 660s. ^1H NMR ($CDCl_3$, 293 K): δ, 0.93t, 1.4m, 1.8m, 1.9m (18H, C_4H_{9Sn}), 6.44 (s, 2H, CH_{2Btm}), 7.97 (s, 2H, CH_{Btm}), 8.41 (s, 2H, CH_{Btm}). ^1H NMR ($CDCl_3$, 293 K): δ, 0.95t, 1.4m, 1.7m, 1.9m (18H, C_4H_{9Sn}), 6.67 (s, 2H, CH_{2Btm}), 8.03 (s, 2H, CH_{Btm}), 8.80 (s, 2H, CH_{Btm}). Λ_m (DMSO, 293 °C): 12.4 μS (1.2×10^{-3} M).

2.2.5. Btm($SnPh_2Cl_2$) ($\mathbf{4_{Btm}}$)

Btm (0.150 g, 1.0 mmol) was added to a methanol solution (20 mL) containing Ph_2SnCl_2 (0.343 g, 1.0 mmol). A colorless precipitate immediately formed. The suspension was stirred for 12 h under N_2 at room temperature. The resulting colorless precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of diethyl ether, recrystallized from ethanol and shown to be compound $\mathbf{4_{Btm}}$ (0.469 g, 0.95 mmol, yield 95%). M.p. 166–167 °C dec. *Anal.* Calc. for $C_{17}H_{16}Cl_2N_6Sn$: C, 41.34; H, 3.26; N, 17.01. Found: C, 41.71; H, 3.20; N, 17.12%. IR (nujol, cm^{-1}): 3117w; 1570w, 1540w, 1518m, 1508m υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 461m, 382w, 291s, 283s, 233s br υ(Sn–Cl). ^1H NMR (DMSO-d_6, 293 K): δ, 6.6, 6.7 (2s, 2H, CH_{2Btm}), 7.2–7.5 (m, 10H, Sn–C_6H_5), 8.0, 8.1 (s, 2H, CH_{Btm}), 8.8, 8.9 (s, 2H, CH_{Btm}). ^1H NMR (CD_3OD, 293 K): δ, 6.66 (2s, 2H, CH_{2Btm}), 7.5 (m, 6H, Sn–C_6H_5, ^1J(Sn–^1H): 103 Hz), 7.9 (m, 4H, Sn–C_6H_5), 8.03 (s, 2H, CH_{Btm}), 8.79 (s, 2H, CH_{Btm}). ^{119}Sn NMR (DMSO-d_6, 293 K), δ: −402 ppm. ^{119}Sn NMR (CD_3OD, 293 K), δ: −241 ppm. Λ_m (DMSO, 293 °C): 32.5 μS (0.4×10^{-3} M).

2.2.6. Btm($SnMeCl_3$) ($\mathbf{5_{Btm}}$)

To a stirred ethanol solution (20 mL) containing $MeSnCl_3$ (0.240 g, 1.0 mmol) Btm (0.150 g, 1.0 mmol) was added. The suspension was stirred for 2 h under N_2 at room temperature. The resulting colorless precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of ethanol and shown to be compound $\mathbf{5_{Btm}}$ (0.220 g, 0.56 mmol, yield 56%). M.p. 257–258 °C dec. *Anal.* Calc. for $C_6H_9Cl_3N_6Sn$: C, 18.47; H, 2.32; N, 21.54. Found: C, 18.65; H, 2.54; N, 21.44%. IR (nujol, cm^{-1}): 3139w, 3110w, 3060sh; 1539s, 1519br υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 536s, 406w, 334s, 289s υ(Sn–Cl). ^1H NMR (DMSO-d_6, 293 K): δ, 1.00 (s br, 3H, CH_{3Sn}), 6.6, 6.7 (br, 2H, CH_{2Btm}), 8.1, 8.15 (s br, 2H, CH_{Btm}), 8.8, 8.9 (s br, 2H, CH_{Btm}). ^1H NMR (DMSO-d_6, 293 K): δ, 0.93 (s, 3H, CH_{3Sn}, $^1J(^{119}Sn–^1H)$: 133 Hz, $^1J(^{117}Sn–^1H)$: 123 Hz), 6.65 (s, 2H, CH_{2Btm}), 8.04 (s, 2H, CH_{Btm}), 8.84 (s, 2H, CH_{Btm}). ^{119}Sn NMR (DMSO-d_6, 293 K): − 450br. Λ_m (DMSO, 293 °C): 13.5 μS (0.6×10^{-3} M).

2.2.7. Btm($SnPhCl_3$) ($\mathbf{6_{Btm}}$)

Bis(triazol-1-yl)methane (Btm) (0.150 g, 1.0 mmol) was added to a ethanol solution (20 mL) containing $PhSnCl_3$ (0.303 g, 1.0 mmol). A colorless precipitate immediately formed. The suspension was stirred for 12 h under N_2 at room temperature. The resulting colorless precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of diethyl ether and 10 mL of methanol and shown to be compound $\mathbf{6_{Btm}}$ (0.350 g, 0.77 mmol, yield 77%). M.p. 250 °C dec. *Anal.* Calc. for $C_{11}H_{11}Cl_3N_6Sn$, C, 29.21; H, 2.45; N, 18.58. Found: C, 28.82; H, 2.42; N, 18.30%. IR (nujol, cm^{-1}): 3114w; 1574w, 1518m υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 450m, 385w, 313s υ(Sn–Cl), 293s, 264sh υ(Sn–C), 232m, 193m. ^1H NMR (CD_3OD, 293 K): δ, 6.67 (s, 2H, CH_{2Btm}), 7.37 (m, 3H, Sn–C_6H_5), 7.84 (m, 2H, Sn–C_6H_5), 8.07 (s, 2H, CH_{Btm}), 8.84 (s, 2H, CH_{Btm}). ^1H NMR (DMSO-d_6, 293 K): δ, 6.5s, 6.6s (br, 2H, CH_{2Btm}), 7.2–7.5 (m, 2H, Sn–C_6H_5), 8.0, 8.1, 8.8, 8.9 (s br, 2H, CH_{Btm}). Λ_m (DMSO, 293 °C): 18.0 μS (0.9×10^{-3} M).

2.2.8. [Btm($Sn^tBu_2Cl_2$)] ($\mathbf{7_{Btm}}$)

Bis(triazol-1-yl)methane (Btm) (0.150 g, 1.0 mmol) was added to a methanol solution (20 mL) containing $^tBu_2SnCl_2$ (0.303 g, 1.0 mmol). The solution was stirred overnight and then slowly evaporated until a colorless precipitate formed which was filtered off and washed with 20 ml of diethyl ether and shown to be compound $\mathbf{7_{Btm}}$ (45% yield). M.p. 143–145 °C dec. *Anal.* Calc. for $C_{13}H_{24}Cl_2N_6Sn$, C, 34.40; H, 5.33; N, 18.51. Found: C, 33.90; H, 5.42; N, 18.89. IR (nujol, cm^{-1}): 3186w, 3111w, 3096w; 1515sh, 1503m υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 391m, 384m, 342s, 272w, 254m, 250m. ^1H NMR (CD_3OD, 293 K): δ, 1.46 (s, 18H, C_4H_{9Sn}, $^1J(^{119}Sn–^1H)$: 117 Hz, $^1J(^{117}Sn–^1H)$: 112 Hz), 6.67 (s, 2H, CH_{2Btm}), 8.03 (s, 2H, CH_{Btm}), 8.79 (s, 2H, CH_{Btm}). ^1H NMR ($CDCl_3$, 293 K): δ, 1.45 (s, 18H, C_4H_{9Sn}, $^1J(^{119}Sn–^1H)$: 117 Hz, $^1J(^{117}Sn–^1H)$: 112 Hz), 6.45 (s, 2H, CH_{2Btm}), 7.97 (s, 2H, CH_{Btm}), 8.45(s, 2H, CH_{Btm}). Λ_m (DMSO, 293 °C): 6.5 μS (1.0×10^{-3} M).

2.2.9. Btm($SnCl_4$) ($\mathbf{8_{Btm}}$)

Bis(triazol-1-yl)methane (Btm) (0.151 g, 1.0 mmol) was added to a dichloromethane solution (20 mL) containing $SnCl_4$ (0.26 g, 1.0 mmol). A colorless precipitate immediately formed. The suspension was stirred for 4 h under N_2 at room temperature. The resulting colorless precipitate was isolated by filtration and dried in vacuum. The residue obtained was washed with 5 mL of dichloromethane, and shown to be compound $\mathbf{8_{Btm}}$ (0.250 g, 0.60 mmol, yield 60%). M.p. 200 °C dec. *Anal.* Calc. for $C_5H_6Cl_4N_6Sn$, C, 14.62; H, 1.47; N, 20.47. Found: C, 15.05; H, 1.78; N, 20.53%. IR (cm^{-1}): 3142w, 3119w, 3027w; 1538m, 1530sh, 1519m, υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 390w, 320s υ(Sn–Cl), 190w, 165m. ^1H NMR (DMSO-d_6, 293 K): δ, 6.63 (s, 2H, CH_{2Btm}), 8.03 (s, 2H, CH_{Btm}), 8.82 (s, 2H, CH_{Btm}). ^1H NMR (DMSO-d_6, 293 K): δ, 6.6, 6.7 (s, 2H, CH_{2Btm}), 8.0, 8.1, 8.8, 8.9, 9.0 (br, 4H, CH_{Btm}).^{119}Sn NMR (DMSO-d_6, 293 K): −625, −668. Λ_m (DMSO, 293 °C): 78.4 μS (0.7×10^{-3} M).

2.2.10. Btm($SnBr_4$) ($\mathbf{9_{Btm}}$)

Btm (0.151 g, 1.0 mmol) was added to a dichloromethane solution (20 mL) containing $SnBr_4$ (0.436 g, 1.0 mmol). A colorless precipitate immediately formed. The suspension was stirred for 4 h under N_2 at room temperature, then filtered off and the precipitate dried in vacuum. The residue obtained was washed with 5 mL of dichloromethane and shown to be compound $\mathbf{9_{Btm}}$ (0.423 g, 0.72 mmol, yield 72%). M.p. 300 °C dec. *Anal.* Calc. for $C_5H_6Br_4N_6Sn$: C, 10.21; H, 1.03; N, 14.28. Found: C, 10.34; H, 1.25; N, 14.65%. IR (nujol, cm^{-1}): 3126w, 3060w; 1608w, 1560w, 1540m υ(C$\overline{\cdots}$C, C$\overline{\cdots}$N), 403w, 392w, 286w, 231s, 221s, 212s υ(Sn–Br). ^1H NMR (CD_3OD, 293 K): δ, 6.79 (s, 2H, CH_{2Btm}), 8.29 (s, 2H, CH_{Btm}), 9.19 (s, 2H, CH_{Btm}). Λ_m (DMSO, 293 °C): 84.0 μS (0.6×10^{-3} M).

2.2.11. $(Btm)_2(Sn^nBu_2Br_2)$ ($\mathbf{10_{Btm}}$)

Bis(triazol-1-yl)methane (Btm) (0.150 g, 1.0 mmol) was added to a dichloromethane solution (20 mL) containing $^nBu_2SnBr_2$ (0.392 g, 1.0 mmol). The solution was stirred overnight. Upon addition of 15 mL of diethyl ether a colorless precipitate formed which was filtered off and washed with 20 ml of *n*-hexane and shown to be compound $\mathbf{10_{Btm}}$ (40% yield). M.p. 108 °C dec. *Anal.* Calc. for $C_{18}H_{30}Br_2N_{12}Sn$, C, 31.20; H, 4.36; N, 24.25. Found: C, 31.57; H, 4.31; N, 24.57%. IR (KBr, cm^{-1}): 3115w, 3027w, 2965w, 2927w, 2857w; 1515m, 1454w, 1408w, 1384w, 1355w, 1268m, 1192m, 1115s, 1026m, 979m, 956m, 908m, 885m, 779m, 731s, 683m, 660s. ^1H NMR ($CDCl_3$, 293 K): δ, 0.92t, 1.4m, 1.8m (18H, C_4H_{9Sn}), 6.44 (s, 4H, CH_{2Btm}), 7.97 (s, 4H, CH_{Btm}), 8.41 (s, 4H, CH_{Btm}). ^1H NMR ($CDCl_3$, 293 K): δ, 0.96t, 1.43m, 1.8m (18H, C_4H_{9Sn}), 6.67

Table 1
Crystal data and refinement details for the compounds $\mathbf{1_{Btm}}$, $\mathbf{4_{Btm}}$ and $\mathbf{5_{Btm}}$ and their Bim counterparts (taken from Ref. [20]).

	$\mathbf{1_{Btm}}$	$\mathbf{4_{Btm}}$	$\mathbf{5_{Btm}}$	$\mathbf{1_{Bim}}$	$\mathbf{5_{Bim}}$
Empirical formula	$C_7H_{12}Cl_2N_6Sn$	$C_{17}H_{16}Cl_2N_6Sn$	$C_6H_9Cl_3N_6Sn$	$C_9H_{14}Cl_2N_4Sn$	$C_8H_{11}C_3N_4Sn$
fw (g mol^{-1})	369.83	493.97	390.25	361.80	450.33
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
SPGR, *Z*	*C*2/*c*, 4	$P2_1/n$, 4	$P\bar{1}$, 2	$P2_1/n$, 4	*C*2, 2
a (Å)	15.2596(4)	12.4477(6)	7.9918(2)	15.333(1)	10.706(2)
b (Å)	11.8545(3)	15.3044(9)	10.5354(2)	9.000(1)	8.217(1)
c (Å)	8.5151(2)	9.8471(5)	8.0486(2)	10.650(1)	8.077(1)
α (°)	90	90	110.531(1)	90	90
β (°)	119.410(2)	90.972(4)	86.187(3)	107.569(3)	67.363(4)
γ (°)	90	90	91.416(2)	90	90
V, Å^3	1341.84(6)	1875.6(2)	633.21(2)	1401.0(1)	655.8(2)
ρ_{calc} (g cm^{-3})	1.83	1.74	2.05	1.71	1.94
μ(Cu Kα) (cm^{-1})	187	136	218	179	210
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)
2θ range (°)	8–105	8–105	7–105	5–105	5–105
M/GOF	67.6	21.6	41.6	18	15
N_{data}	4851	4851	4901	5001	5001
R_p, R_w	0.093, 0.125	0.086, 0.120	0.058, 0.077	0.053, 0.153	0.015, 0.095
R_{Bragg}	0.084	0.103	0.043	0.052	0.038
V/*Z* (Å^3)	335	469	316	350	328

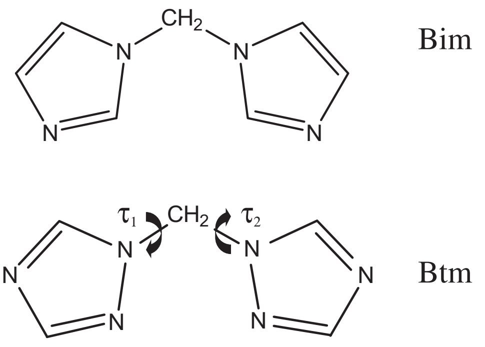
(s, 4H, CH_{2Btm}), 8.03 (s, 4H, CH_{Btm}), 8.80 (s, 4H, CH_{Btm}). Λ_m (DMSO, 293 °C): 24 μS (1.0 × 10^{-3} M).

2.2.12. BtmSn^{n}Bu$_2$(NO$_3$)$_2$ ($\mathbf{11_{Btm}}$)

Bis(triazol-1-yl)methane (Btm) (0.150 g, 1.0 mmol) was added to a dichloromethane solution (20 mL) containing $^nBu_2Sn(NO_3)_2$ (0.356 g, 1.0 mmol). A colorless precipitate formed which was filtered off and washed with diethyl ether and shown to be compound $\mathbf{11_{Btm}}$ (60% yield). M.p. 190 °C dec. *Anal.* Calc. for $C_{13}H_{23}N_8O_6Sn$, C, 30.85; H, 4.58; N, 22.14. Found: C, 30.77; H, 4.31; N, 22.34%. IR (KBr, cm^{-1}): 3139w, 3036w, 2964w; 2930w, 2864w; 1517m, 1484s, 1457m, 1382m, 1270s, 1200m, 1116s, 1032m, 996m, 981m, 959m, 884br, 812w, 781m, 728m, 687m, 670s. ^{1}H NMR $(CD_3)_2CO$, 293 K): δ, 0.83t, 1.31m, 1.6m, 1.88m (18H, C_4H_{9Sn}), 6.44 (s, 4H, CH_{2Btm}), 7.97 (s, 4H, CH_{Btm}), 8.41 (s, 4H, CH_{Btm}).

2.3. X-ray powder diffraction studies

Diffraction data of all powder specimens were measured at room temperature, in air. Unfortunately, only a few (**1**, **4** and **5**) gave XRPD traces of decent quality, allowing a fruitful structural determination (as reported hereafter), while the remaining ones, even after different syntheses and preparations, did not afford interpretable diffraction traces. Among these, we were able to detect the lattice parameters of **3** and, perhaps, **6**, but not to fully unravel their crystal structure [38].



Scheme 1.

Strictly monophasic samples of **1**, **4** and **5** were gently ground in an agate mortar, and then deposited in the hollow of a 0.2 mm deep aluminum sample holder, equipped with a quartz monocrystal zero background plate (supplied by *The Gem Dugout*, State College, PA). Diffraction data were collected in the 5–105° 2θ range, sampling at 0.02°, on a θ:θ vertical scan Bruker AXS D8 Advance diffractometer, equipped with a linear Lynxeye position sensitive detector, set at 300 mm from the sample. Ni-filtered Cu K$\alpha_{1,2}$ radiation, λ = 1.5418 Å. Standard peak search methods, followed by indexing by TOPAS-R [39], allowed the determination of approximate cell parameters; systematic absences allowed the detection of the probable space groups (see Table 1), later confirmed by successful structure solutions and refinements. Structure solution was initiated by employing a semi-rigid molecular fragment for Btm, flexible about two torsion angles (see Scheme 1), and free tin and chloride atoms. Where pertinent, alkylic or aromatic residues were added as further independent groups. Hydrogen atoms have been positioned in idealized locations, as they have been included in the definition of the rigid bodies. If the Btm molecule was found to be bisected by a twofold axis, only a rigid portion of the molecule was employed. Simulated annealing (occasionally helped by soft restraints) allowed the location and orientation of the used fragments, later refined by the Rietveld method. The fundamental parameter approach in describing the peak shapes was employed, the background contribution was modeled by a polynomial fit, and preferred orientation effects for **4** (0 1 0 pole) were described by the March–Dollase formulation [40]. A single isotropic thermal parameter was adopted for the Sn atoms, while lighter atoms were assigned $B = B_{Sn} + 2.0$ Å^2. Fig. 1 shows the final Rietveld refinement plots, with peak markers and difference plot at the bottom [41]. Structure solution and refinements were performed by TOPAS-R. Crystal data, data collection parameters and agreement factors are shown in Table 1. The indexed XRPD trace and the pertinent Pawley fit for species **3** (in *C*2/*c*) is supplied in Fig. 2, where the presence of a still unknown crystalline contaminant is evident.

3. Results and discussion

3.1. Synthesis and spectroscopy

The reaction between diorganotin(IV) compounds R_2SnX_2 and an equimolar quantities of Btm in organic solvent (ethanol, methanol or dichloromethane) produces, in moderate yields, the

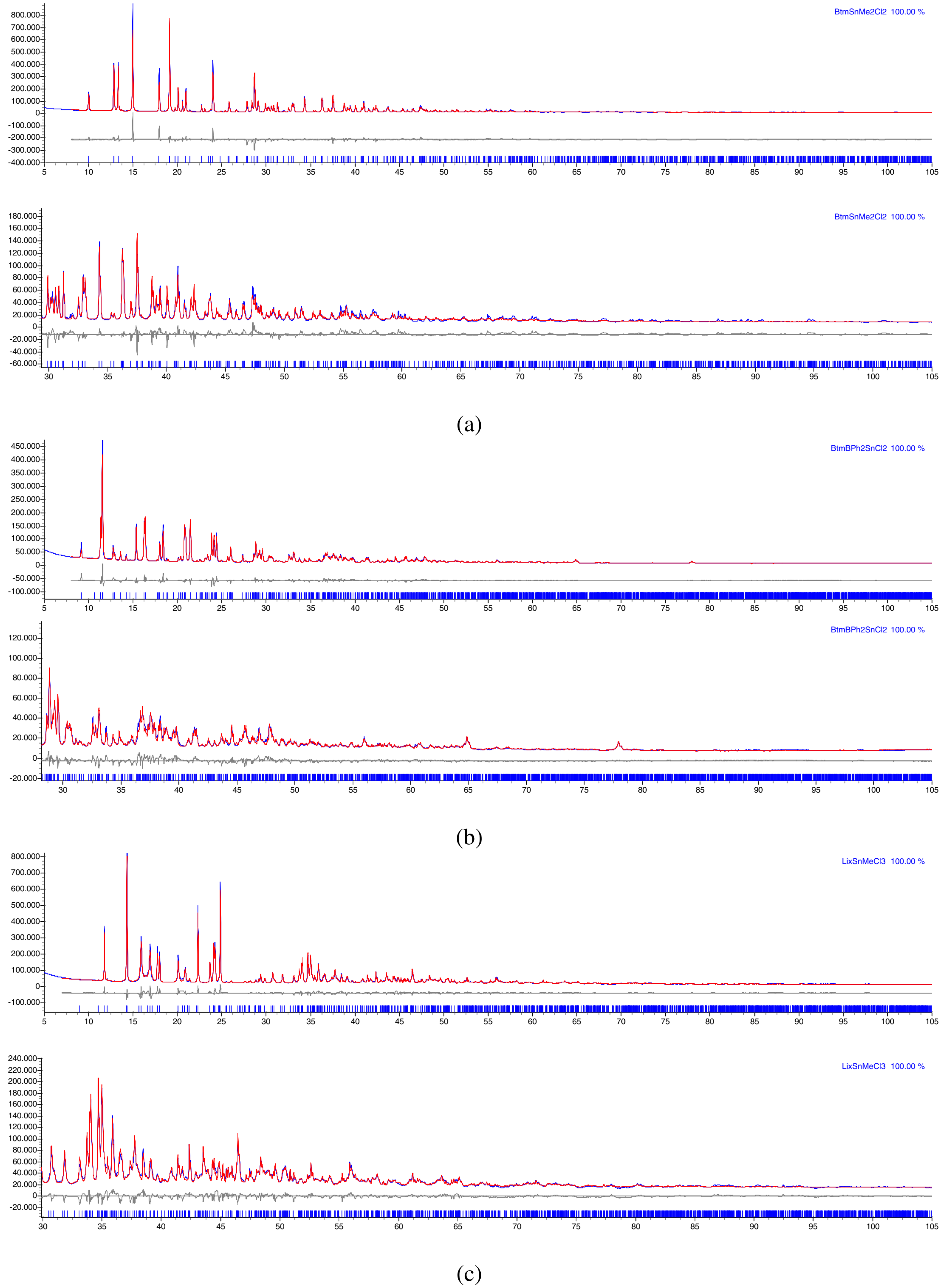


Fig. 1. Rietveld refinement plots for species $\mathbf{1}_{\mathbf{Btm}}$ (a), $\mathbf{4}_{\mathbf{Btm}}$ (b) and $\mathbf{5}_{\mathbf{Btm}}$ (c) with difference plots and peak markers at the bottom. The lowest portions show the high-angle range at a magnified scale (5×).

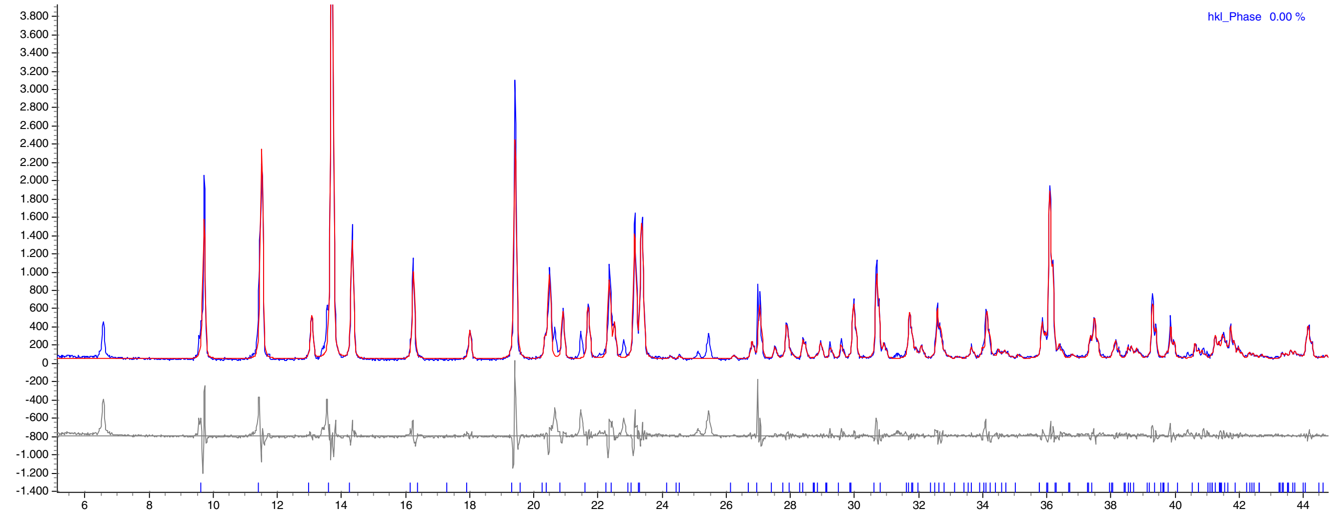


Fig. 2. Pawley fit for species $\mathbf{3_{Btm}}$, with difference plot and peak markers at the bottom. The presence of reflections from a yet unknown contaminant phase is obvious.

compounds Btm(R_2SnX_2) $\mathbf{1_{Btm}}$–$\mathbf{4_{Btm}}$ and $\mathbf{7_{Btm}}$ listed in Section 2. The formation of these species requires long times and higher concentrations of the reactant, the products being moderately soluble in the reaction solvents. The 2:1 adduct $\mathbf{10_{Btm}}$ (Btm)$_2$(R_2SnBr_2) formed in the same conditions also when the reaction was carried out in a strong excess of the organotin species. Derivatives $\mathbf{1_{Btm}}$, $\mathbf{3_{Btm}}$, $\mathbf{4_{Btm}}$ and $\mathbf{10_{Btm}}$ were obtained upon addition of diethyl ether to the reaction solution, whereas $\mathbf{2_{Btm}}$ and $\mathbf{7_{Btm}}$ formed upon slow evaporation of the reaction solvent. The reaction between Btm and $RSnX_3$ or SnX_4 immediately afforded colorless insoluble precipitates of Btm($RSnX_3$) $\mathbf{5_{Btm}}$–$\mathbf{6_{Btm}}$ or Btm(SnX_4) $\mathbf{8_{Btm}}$–$\mathbf{9_{Btm}}$ in high-yield, independently on the solvent employed. No adduct has been obtained by reacting, in the same reaction conditions, the donor Btm with R_3SnX, probably because of the +I effect of the organic residues, diminishing the Lewis acidic character of the Sn(IV) center. Finally the derivative $\mathbf{11_{Btm}}$ has been prepared only when Btm was reacted with ^{n}Bu$_2$Sn(NO$_3$)$_2$, previously prepared. On the other hand when Btm(R_2SnX_2) was reacted with AgX (X = NO_3 or ClO_4), only untreatable materials or the starting reactants were recovered from the reaction mixtures.

All obtained compounds, $\mathbf{1_{Btm}}$–$\mathbf{11_{Btm}}$, are colorless solids, sufficiently stable to air and soluble only in DMSO, acetone and sometimes also in CD_3OD and $CDCl_3$. The conductivity measurements in DMSO and/or acetone suggest partial ionic dissociation into the starting reagents for $\mathbf{1_{Btm}}$–$\mathbf{7_{Btm}}$ and $\mathbf{10_{Btm}}$, whereas the tin adducts $\mathbf{8_{Btm}}$ and $\mathbf{9_{Btm}}$ behave in DMSO as 2:1 electrolytes.

The IR data are also reported in Section 2. All the spectra show very weak vibration bands at *ca.* 3000 cm^{-1} that can be assigned to the ν(CH) of the heterocyclic ring, whereas a more intense absorption band at *ca.* 1600 cm^{-1} is likely due to ring breathing [42]. Most IR absorptions are slightly shifted with respect to the corresponding absorptions in the free Btm. We have also compared the far-IR spectra of the complexes $\mathbf{1_{Btm}}$–$\mathbf{4_{Btm}}$, $\mathbf{7_{Btm}}$ and $\mathbf{10_{Btm}}$ with that of the uncomplexed Btm, so that it has been possible to assign the strong band found in $\mathbf{1_{Btm}}$, falling near 575 cm^{-1}, to ν_{asym} Sn–C [43,44], whereas the two strong absorptions found in $\mathbf{4_{Btm}}$ at 291 and 282 cm^{-1} suggest a markedly distorted *trans*-R_2 distorted octahedral diphenyltin(IV) complex [45,46]. In $\mathbf{3_{Btm}}$ and $\mathbf{4_{Btm}}$, the Sn–C stretching absorption bands are found at *ca.* 620 cm^{-1}. Upon comparing the low-lying Sn–Cl stretching frequencies in di- (240 cm^{-1}), tri- (330–290 cm^{-1}) and tetrachloride (320 cm^{-1}) complexes with those of the starting tin(IV) and organotin(IV) species [47], significant shifts to lower frequency are found, in full agreement with the trend previously described for other analogous complexes [48].

The ^{1}H NMR spectra of derivatives $\mathbf{1_{Btm}}$–$\mathbf{4_{Btm}}$ and $\mathbf{7_{Btm}}$ in chloroform, methanol or DMSO support the formulae proposed and show that the organic ligand has not undergone any structural change upon complexation. However, these spectra also show that these polymeric complexes are completely dissociated in solution, since only negligible differences exist between the chemical shifts of the free ligand and those of the dissolved complexes. Furthermore, in the case of the trihalide and tetrahalide species, not soluble in $CHCl_3$, the spectra in DMSO or MeOH show sensible dependence on the dilution: indeed, at low concentrations, very close coincidence between the proton chemical shifts of the free ligand and of the dissolved complexes, is observed, whereas, at higher concentrations, the number of signals increases, suggesting the occurrence of equilibria such as:

$$\text{“Btm(RSnX}_3\text{)”} + x\text{DMSO} = \text{RSnX}_3(\text{DMSO})_x + \text{“Btm”}$$

in which the elusive “Btm($RSnX_3$)” fragment is generated by uncomplete disruption of the organometallic polymer or, vice versa, by formation of oligomeric fragments based on the Btm–Sn(IV) bond. The ^{119}Sn NMR data, reported only for some selected compounds, due to the low solubility of the species show that the dimethyl and diethyltin(IV) chloride are comparable with that of the corresponding Lewis acid in the same solvent and clearly indicate that this type of complexes is extensively dissociated in solution [49]. On the other hand the ^{119}Sn NMR spectra of the tri- and tetrahalide tin complexes in CD_3OD, acetone-d_6 and DMSO-d_6 [50] indicates that this strong solvating species are able to displace the Btm from the tin coordination sphere.

3.2. Crystal chemistry

Crystals of $\mathbf{1_{Btm}}$, $\mathbf{4_{Btm}}$ and $\mathbf{5_{Btm}}$ share the presence of one-dimensional polymeric chains based on the Btm–Sn–Btm–Sn sequence generated by exobidentate Btm ligands, which link differently substituted organometallic Sn(IV) centers of pseudooctahedral coordination geometry. Portions of the polymeric chain of $\mathbf{1_{Btm}}$ and $\mathbf{1_{Btm}}$ are shown in Figs. 3 and 4, respectively [51]. These chains are invariably isooriented, and parallelly packed in all species, no matter what crystal lattice and space group symmetry are adopted by the overall 3D structure; however, the different nature, size and geometry of the ancillary ligands modulate their

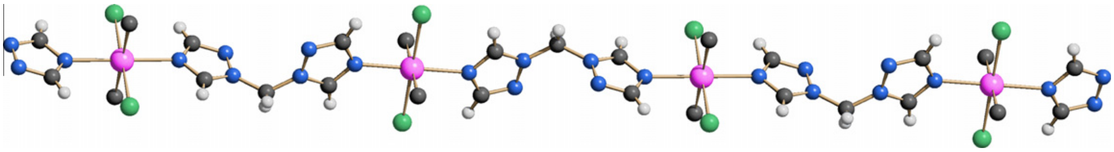


Fig. 3. Schematic drawing of the polymeric chain present in compound $\mathbf{1_{Btm}}$.

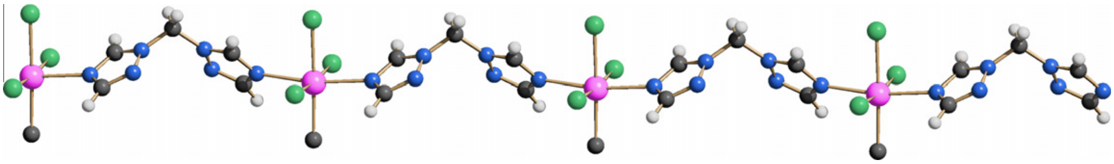


Fig. 4. Schematic drawing of the polymeric chain present in compound $\mathbf{5_{Btm}}$.

Table 2
Synoptic collection of relevant structural and stereochemical features of the compounds $\mathbf{1_{Btm}}$, $\mathbf{4_{Btm}}$, $\mathbf{5_{Btm}}$, $\mathbf{1_{Bim}}$, $\mathbf{5_{Bim}}$ and Btm(Ph_2SnBr_2).

	$\mathbf{1_{Btm}}$	$\mathbf{4_{Btm}}$	$\mathbf{5_{Btm}}$	$\mathbf{1_{Bim}}$	$\mathbf{5_{Bim}}$	Btm(Ph_2SnBr_2)
Ref.	This work	This work	This work	[20]	[20]	[36]
Topology	1D	1D	1D	1D	1D	1D
Geometry	octahedral	octahedral	octahedral	octahedral	octahedral	octahedral
Coordination	$N_2C_2Cl_2$ *trans*-N,N *trans*-C,C *trans*-Cl,Cl	$N_2C_2Cl_2$ *cis*-N,N *trans*-C,C *cis*-Cl,Cl	N_2CCl_3 *trans*-N,N *mer*-Cl,Cl,Cl	$N_2C_2Cl_2$ *trans*-N,N *trans*-C,C *trans*-Cl,Cl	N_2CCl_3 *trans*-N,N *mer*-Cl,Cl,Cl	$N_2C_2Br_2$ *cis*-N,N *trans*-C,C *cis*-Br,Br
Sn–N (Å)	2.237(2)	*2.53-2.55*	2.24(2)-2.33(2)	2.31-2.32	2.29	2.45
Sn–Cl (Å)	2.458(7)	2.678(4)-2.692(3)	*2.42-2.45*	2.43-2.45	2.28, 2.49	2.62
Sn–C (Å)	*2.15*	*2.15*	*2.20*	2.12-2.20	2.29	2.15
Sn–Btm–Sn (Å)	11.21	9.85	10.78	11.09	10.64	9.57
N–Sn–N (°)	180	100.8(4)	169.8(4)	180	173.4	88.2
Idealized Btm symmetry	C_2	C_s	C_2	C_2	C_2	C_s
Sn site symmetry	−1	1	1	−1	2	m

relative arrangement in the orthogonal plane, thus the 2D packing of the polymeric chains. Another interesting versatility element is the conformational flexibility about the two N–CH_2 bonds, already present in the Bim analogs, and, differently from these recently published cases, the possibility of linkage isomerization, given that Btm is a multitopic nitrogen ligand. In the following, a comparative structural analysis is presented between Bim and Btm couples, highlighting analogies, and, more fascinatingly, the most peculiar differences, while the relevant stereochemical features of these new species are synoptically collected in Table 2.

3.2.1. Crystal structures of $\mathbf{1_{Btm}}$ and $\mathbf{5_{Btm}}$

These two compounds, Btm(Me_2SnCl_2) and Btm($MeSnCl_3$), are expected to be isostructural, thanks to the substantial similarity of the isosteric methyl and chlorine ligands. While this is nearly true in terms of molecular geometry and overall chain conformation, their crystal packing is substantially different.

Indeed, Btm(Me_2SnCl_2) crystallizes in the $C2/c$ space group, with the metal atom lying in the −1 special position and the Btm ligand bisected by a twofold axis. This implies that the Btm ligand adopts the nearly ubiquitous [for Sn(IV) polymers] C_2 conformation, as in $\mathbf{1_{Bim}}$, even if the lattice parameters speak for a non-isomorphous character of the two derivatives. This difference can be traced back to the different lengths of the bridged Sn···Sn interactions (11.09 and 11.21 Å, in $\mathbf{1_{Bim}}$ and $\mathbf{1_{Btm}}$, respectively) and, particularly, to the (approximate) [0 0 1] and [1 0 2] orientation of the chains in the two (nearly isooriented) monoclinic lattices. Interestingly, the disorder affecting the crystal structure of $\mathbf{1_{Bim}}$ (the mutual interchange of the nearly isosteric methyl and chloride residues) could be easily ruled out from our XRPD analysis in $\mathbf{1_{Btm}}$, thus clearly indicating the *trans* $N_2C_2Cl_2$ stereochemistry at the metal. The absence of disorder is also partially reflected by the significantly lower molar volume of $\mathbf{1_{Btm}}$, about 15 $Å^3$ smaller than in $\mathbf{1_{Bim}}$.

At variance from $\mathbf{1_{Btm}}$, Btm($MeSnCl_3$), $\mathbf{5_{Btm}}$, is triclinic, $P\bar{1}$, with the metal atom lying in general position, as well as all other atoms in the structure do. Also in this case the Btm ligand adopts a C_2 conformation, as in $\mathbf{5_{Bim}}$, but with markedly distinct lattice parameters, space group symmetry and site symmetry location of the metal atom (bisected by a twofold axis in $\mathbf{5_{Bim}}$). Slightly different bridged Sn···Sn interactions (10.64 and 10.78 Å, in $\mathbf{5_{Bim}}$ and $\mathbf{5_{Btm}}$, respectively) in these non-isomorphous species are observed, both significantly lower than those present in the dimethyl derivatives $\mathbf{1_{Bim}}$ and $\mathbf{1_{Btm}}$, discussed above. Also in the case of $\mathbf{5_{Btm}}$, no disorder was observed among the methyl and chlorine ligands. Additionally, also in this case, a slightly denser phase is observed, with a *ca.* 10 $Å^3$ smaller molar volume than $\mathbf{5_{Bim}}$.

3.2.2. Crystal structure of $\mathbf{4_{Btm}}$

Species Btm(Ph_2SnCl_2), $\mathbf{4_{Btm}}$, crystallizes in the monoclinic space group $P2_1/n$ with all atoms lying in general position. Also in this case, a 1D polymeric chain is present (see Fig. 5), built by pseudooctahedral $SnC_2N_2Cl_2$ centers (with a rare *trans* C–C, *cis*-N,N and *cis*-Cl,Cl stereochemistry) which, connected through the Btm bridges, lie approximately 9.45 Å apart. As in the already known bromine analog, Btm(Ph_2SnBr_2) [36], the two phenyl rings, attached to the same Sn(IV) atoms, show a staggered conformation.

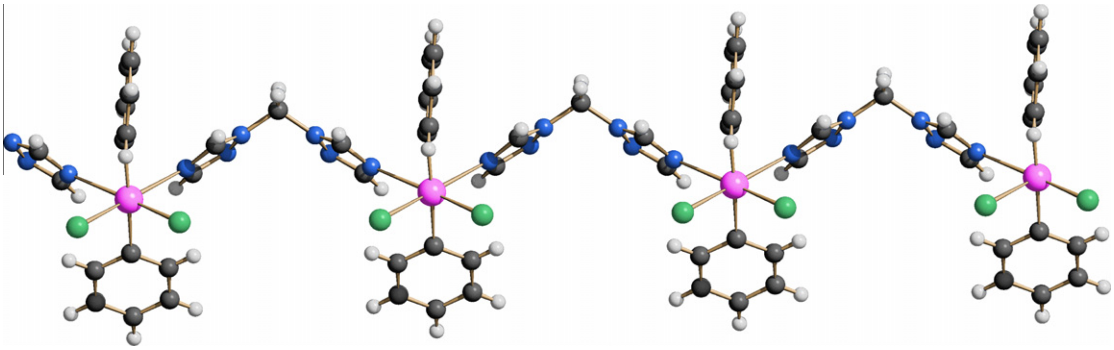


Fig. 5. Schematic drawing of the polymeric chain present in compound $\mathbf{4_{Btm}}$.

Despite of this similarity, and of the common C_s symmetry of the Btm ligand in the two Btm(Ph_2SnX_2) (X = Cl, Br) species, the two crystals adopt different crystal systems, but are related by a proper group-subgroup relation, the bromine derivative possessing higher symmetry (*Pnma* vs. $P2_1/n11$, once reorientation of the cell axes is allowed), with the two phenyls bisected (in different ways!) by one mirror plane. As expected, also the Sn···Sn are similar [9.57 Å in Btm(Ph_2SnBr_2)], and reflect the larger size of the halide in the latter species.

4. Conclusions

The present paper reports on the preparation and characterization of a number of Sn(IV) one-dimensional polymers containing the rarely studied bis-(1,2,4-triazolyl) ligand. Of the several materials prepared, listed above, only three afforded easily interpretable powder diffraction data, and allowed the retrieval of a coherent structural model. However, even in these fortunate cases, the quality of the XRPD traces (in terms of peak widths and shape) and the large scattering of the dominant metal atom required the use of rigid body models and the introduction of geometrical restraints (as an ancillary set of "observations"). Accordingly, the final picture of the structural models is somewhat blurred, particularly if compared with the large set of structural information previously retrieved by us on the Sn(IV) polymers containing the bis-imidazolyl analog. Nevertheless, the overall topology, stereochemistry and intermetallic distances are well defined, and could be successfully compared with those of other Btm or Bim derivatives, highlighting the non-isomorphous character of the selected couples.

Why for the Btm derivatives the (well defined) analytical data do not match with equally good powder diffraction traces (which, in some cases, contain unindexable peaks, or show very poor crystallinity) is not yet understood. We tentatively put forward the hypothesis that, in the solid, linkage-isomers of the Btm ligand (possessing different donor sites) may exist, disrupting the ideal crystalline periodicity. Perhaps, only solid-state NMR may help in assigning such variability, which solution (multinuclear) NMR experiments alone could not detect: indeed, once dissolved in polar and coordinating solvents, it is likely that, as described above, only low-mass (monomeric?) complexes exist, thus limiting the power of the spectroscopic information derived therefrom.

5. Supplementary material

CCDC 767916, 767917 and 767918 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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[38] Even if in $\mathbf{3}_{\mathbf{Btm}}$ we evidenced the existence of *trans*-$SnN_2C_2Cl_2$ pseudooctahedral fragments linked to each other in 1D polymeric chains running parallel to $[\bar{1}01]$ in the monoclinic *C*2/*c* cell, and with intermetallic distances (Btm bridged) of *ca.* 10.15 Å. Crystal data: $C_{13}H_{24}Cl_2N_6Sn$, monoclinic, *C*2/*c*, *Z* = 4; *a* = 14.12, *b* = 12.43, *c* = 11.36 Å, *b* = 105.1, *V* = 1925 $Å^3$, ρ = 1.57 g cm^{-3}. A partial structural model indicated the presence of Sn in 0.25, 0.25, 0.0, and Cl in 0.173, 0.689, 0.283, with the Btm ligand bisected by a twofold axis. The apparently large molar volume of this species can in principle be attributed to the large conformational freedom suffered by alkylic, vs. arylic residues, as in $\mathbf{4}_{\mathbf{Btm}}$.

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[51] Worthy of note, no evidence for isostructural couples of the Bim and Btm Sn(IV) polymers were observed, nor polymorphic species could be detected.